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Advancing *In situ* Analytical Electron Microscopy for Probing Dynamic Nano-Scale Solid State Electrochemistry

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In situ analytical electron microscopy (AEM) is a fast-growing and fascinating area of research that has drawn tremendous attention from various fields ranging from materials science to chemistry and biology. In fundamental studies of energy storage system, particularly electrochemical energy storage (EES), *ex situ* experiments often have limited time-scale resolution due to sample preparation and transfer, preventing the determination of the time constant of a reaction/transformation. More importantly, electrochemical systems often operate at states far from equilibrium. On the other hand, the EES systems' macroscopic properties such as the energy and power density are often governed the electrode/electrolyte interfaces that by nature are of atomic and nano scales. Therefore, *in situ* AEM provides great opportunities to characterize dynamic changes in morphology, electronic bonding state, and chemical composition in materials at and below the nanoscale. *In situ* electrochemical operation in the ultra-high vacuum column of a TEM has been pursued by three major strategies (**Fig. 1**). Our team has focused on the solid state approach (2 in Fig.1), where a full cell “nanobattery” can be fabricated from an all-solid-state thin film battery using a set of fully optimized focused ion beam (FIB) fabrication procedure.

Our methodology is at the forefront of this particular strategy by fully enabling galvanostatic cycling of FIB processed cross-sections in the TEM [1]. Galvanostatic biasing, as opposed to using potentiostatic biasing commonly seen in the literature [2-4], provides a powerful and precise control over the state of charge (e.g. Lithium content) at which we can characterize the electrochemical system as a function of states of charge. We established our *in situ* TEM methodology using a model system of lithium cobalt oxide (LCO) cathode, lithium phosphorus oxynitride (LiPON) electrolyte, and amorphous silicon (a-Si) anode all-solid-state battery [5,6]. Alternatively, $\text{Li}(\text{NiMn})_2\text{O}_4$ spinel structures are promising because they allow for three-dimensional Li diffusion. For phase pure $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_4$ the redox couple switches from Mn^{3+} - Mn^{4+} to Ni^{2+} - Ni^{4+} raising the voltage up to 4.7 V [6]. However, these new materials development has been dominated mostly by liquid electrolytes such as carbonate based electrolytes, whose thermal stability and electrochemical stability are poor at high voltages more than 4.5V. Our approach of exploring the compatibility of these high voltage materials with solid electrolytes will open up a new venue for exploring strategies to enable ultra-high energy density EES (doubling or tripling the energy density).

Building off of the *in situ* TEM analysis of the model LCO/LiPON/a-Si battery, we moved forward to analyze the LNMO/LiPON/a-Si system. We have successfully fabricated an electrochemically active LNMO/LiPON/a-Si micro-battery through close collaboration between

UCSD and ORNL. Preliminary results indicate that the LNMO/LiPON interface is more stable than that of LCO/LiPON (**Fig 2.**), however the exact atomistic level understanding is still lacking. As a preliminary study, we have looked at the Spinel-LNMO/LiPON interface and observe that there is no evidence of a disordered interfacial layer that forms. Such a new interface is drastically different from what we previous seen. If we can understand why certain interfaces do not form decomposition interfaces, we can use the knowledge learned in order to form guiding principles of interfacial engineering that produce distinct electrode-electrolyte interfaces with an additional protection layer. Such knowledge would be greatly useful in designing the next generation of all-solid-state thin film batteries and electrode coatings design for bulk systems.

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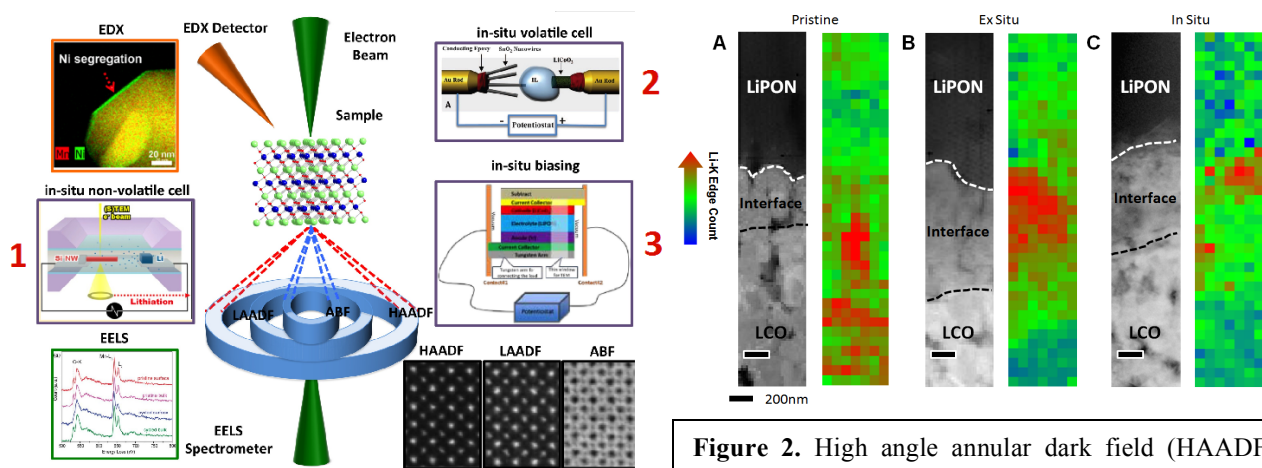


Figure 1. State-of-the-art (S)TEM techniques and their applications in battery research. (Publication 1)

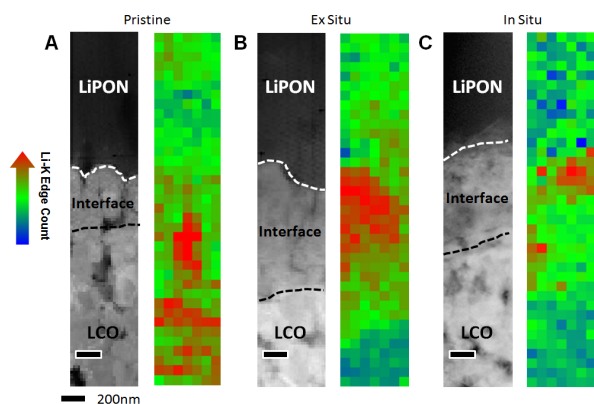


Figure 2. High angle annular dark field (HAADF) and Li-K edge concentration mapping of (a) pristine, (b) *ex situ*, (c) *in situ* thin film battery charged samples between the LCO and LiPON interface.